

Review

Nipponium as a new element ($Z = 75$) separated by the Japanese chemist, Masataka Ogawa: a scientific and science historical re-evaluation

By H. Kenji YOSHIHARA^{*1,†}

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Abstract: This review article deals with a new element ‘nipponium’ reported by Masataka Ogawa in 1908, and with its scientific and science historical background. Ogawa positioned nipponium between molybdenum and ruthenium in the periodic table. From a modern chemical viewpoint, however, nipponium is ascribable to the element with $Z = 75$, namely rhenium, which was unknown in 1908. The reasons for this corrected assignment of nipponium are (1) its optical spectra, (2) its atomic weight when corrected, (3) its relative abundance in molybdenite, the same being true with rhenium. Recently some important evidence was found among the Ogawa’s personal collection preserved by his family. Deciphering the X-ray spectra revealed that the measured spectra of the nipponium sample that Ogawa brought from University College, London clearly showed the presence of the element 75 (rhenium). Thus was resolved the mysterious story of nipponium, which had continued for almost a century. It is concluded that nipponium was identical to rhenium.

Keywords: nipponium, Masataka Ogawa, successful separation of rhenium, William Ramsay, history of discovery of elements, periodic table of chemical elements

1. Introduction

Discovery of the chemical elements has been a subject of prime importance in chemical research. Much instructive and laborious work was performed by a number of discoverers as summarized in several histories.^{1),2)}

All of the naturally occurring elements were known by 1925 when Noddack and coworkers³⁾ found rhenium, the last stable element in nature, with an atomic number Z of 75. Then, the discovery of artificial elements followed. The first cyclotron-produced element with an atomic number $Z = 43$ (1937) was technetium⁴⁾ which was named by Segrè, as a discoverer of this element. The existence of both the elements 43 and 75 was predicted by Mendeleev in his periodic table of chemical elements in 1871.⁵⁾ He placed them in the column of

VII group elements. Many researchers had tried to discover them, but their efforts had been in vain, before the final success attained by the above discoverers.

While the success of a group of Japanese researchers in the production of a new element $Z = 113$ ⁶⁾ is a subject which deserves applause, the ‘discovery of nipponium’ by the Japanese chemist Masataka Ogawa in 1908 is also so worthy, because it was the first challenge to the discovery of any element by a Japanese researcher.

As is described later, Ogawa succeeded in the separation of nipponium for the first time, but incorrectly put it in the position of the present technetium (Tc, $Z = 43$) in the periodic table of chemical elements. Its correct position should have been just under technetium, that is, in the position of rhenium. Ogawa’s mistake became known when X-ray spectroscopy measurements were made on his nipponium sample before his sudden death in 1930, but the findings were not published.

^{*1} Professor Emeritus, Tohoku University, Miyagi, Japan.

[†] Correspondence should be addressed: K. Yoshihara, Kusakidai 4-12-13, Iwaki City, Fukushima 972-8301, Japan (e-mail: kenji-yoshihara@nifty.com).

2. William Ramsay, a giant in the history of discovery of chemical elements

William Ramsay (1852–1916) is very famous for his discovery of the rare gas elements. He was awarded the Nobel Prize in Chemistry in 1904.

Travers,⁷⁾ a member of Ramsay's staff at University College, London, evaluated him highly as an excellent experimentalist. Ramsay's skill in making and handling glassware apparatus helped him to overcome experimental difficulties in the study of rare gas elements. He was of friendly nature and often cooperated with other scientists beyond chemistry. He was fluent in several foreign languages, making many friends outside of his mother country.

In 1894, Ramsay discovered argon in cooperation with Lord Rayleigh (Fig. 1). Other rare gases, krypton, neon and xenon were discovered by Ramsay and Travers in 1898. Helium was observed by Lockyer and Janssen in the sun, but firmly discovered in tiny bubbles in ores containing uranium and thorium in 1895 by Ramsay. Radon was discovered by Rutherford (Nobel Prize 1908) and Owens in 1899, and Ramsay confirmed that radon is a member of the rare gas group elements. Ramsay worked with Soddy (Nobel Prize 1921) and proved by optical spectrum observation that disintegration of radium produces radon and helium. Thus, Ramsay contributed to establishment of the disintegration law. In short, Ramsay was a great master of rare gases.

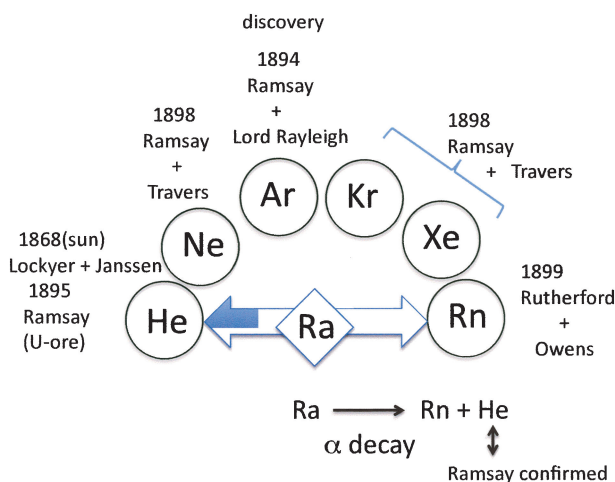


Fig. 1. Discovery of rare gases and Ramsay's participation.

The author wishes to point out another activity which was forgotten or neglected in Ramsay's biography.⁷⁾ He was very interested in the mineral thorianite in which he expected various new elements would be found. This mineral was found in Ceylon (present day Sri Lanka) in 1904, and was noticed for its strange cubic shape, and for its composition which included thorium, uranium, and rare earths. According to a letter⁸⁾ written by Masataka Ogawa, when he visited Ramsay in 1904, Ramsay told him that two 'new elements' were found in thorianite. So, Ogawa decided to stay at Ramsay's laboratory to study the new elements in the mineral. The number of the expected new elements increased over the course of the study. Ramsay⁹⁾ asked Ogawa to give part of his processed fraction from thorianite to Miss Evans to study as one more expected new element. Figure 2 summarizes Ramsay-Ogawa expectations in the four new elements in thorianite. Though their expectations were not totally correct, surprisingly, three of the elements were present as eventually discovered later. The reasoning behind these expectations is not clear, but Ramsay might have done preliminary tests on his samples using optical spectroscopy. It appears that Hahn (Nobel Prize 1944) offered him information on radioactive materials, though related details are not known today.

3. Masataka Ogawa initiated nipponium work at University College, London

A short introduction of Masataka Ogawa (1865–1930) will be given here. He was born in Edo (present day Tokyo). Due to the Meiji Reformation (1868) his family moved to Matsuyama where his father died when Ogawa was young. After he graduated Matsuyama Middle School, he entered the Imperial University of Tokyo with financial support from the former Lord of Matsuyama District. He graduated from the university in 1889 and remained there for graduate school, studying under the guidance of E. Divers, an inorganic chemist (later, the President of the Society of Industrial Chemistry). Then, Ogawa served as a teacher at Shizuoka Middle School for some years. However, strongly wishing to study chemistry further, he went back to his home laboratory, working with Divers again. He obtained the post of professor at the First High School in Tokyo in 1899.

He was sent by the Japanese Government to

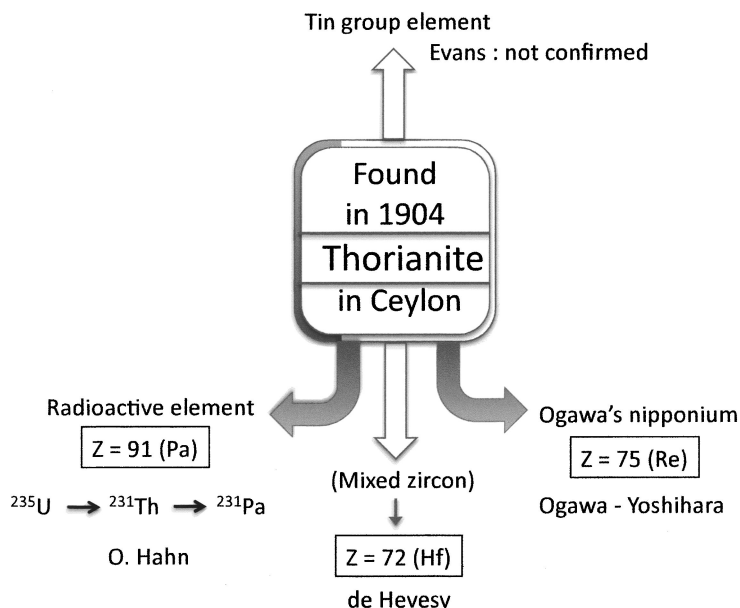


Fig. 2. New elements expected in thorianite.

England to study inorganic chemistry in 1904. He intended to stay at Ramsay's laboratory, University College, London. His first visit to Ramsay was described in the previous section. At that time, Ogawa was given a sample of thorianite, and he started to look for the new elements expected to be contained in it.

After some preliminary experiments, he applied the chemical separation procedures for thorianite shown in Fig. 3.¹⁰⁾ It was laborious and troublesome work to exclude a large enough amount of the main components to extract minor elements, with the final aim of separating out of a new element. Ogawa worked hard day and night. The Russo-Japanese War (1904–05) was being fought in Manchuria at that time. Near the end of 1904 Ramsay tried to encourage Ogawa saying: "Which will be sooner your success in discovering a new element or a Japanese Army's victory at Port Arthur?"

The new element was almost in his hands. Its optical spectrum was characterized with new lines which did not belong to any other known elements. Ogawa was convinced he had discovered a new element, but he could not decide its position in the periodic table of chemical elements. It could be determined by an exact measurement of its atomic weight. However, the problem was that the quantity, which needed to be weighed with high accu-

racy, was very small. So he gathered thorianite from a large amount of factory waste, and applied to it the same procedures to get more of the element.

Finally he subjected a quantity on the order of 0.1 g to determining its equivalent weight using the following procedure:

- (1) conversion of chloride to oxide;
- (2) conversion of oxide to hydroxide to oxide cycle; and
- (3) conversion of sulfate to oxide.

The procedure yielded about 50 as its equivalent weight. Ogawa's initial plan to stay in Europe was for two years, but this was not enough time to accomplish all his work. Ramsay recommended that he extend his stay for six more months and kindly asked permission for Ogawa to do so from the Japanese Government through Ambassador Hayashi in December, 1905.¹¹⁾ In his letter to Hayashi, Ramsay wrote: "Now he is engaged in very interesting work; he has discovered a new element, and is engaged in determining its atomic weight, mapping its spectrum, and finding the properties of its salts."

This comment on Ogawa's work shows how much Ramsay trusted him. The proposed extension of his stay was granted.

Then, in August of 1906 Ogawa went back to Japan bringing, with Ramsay's permission, the separated sample of the new element. He moved

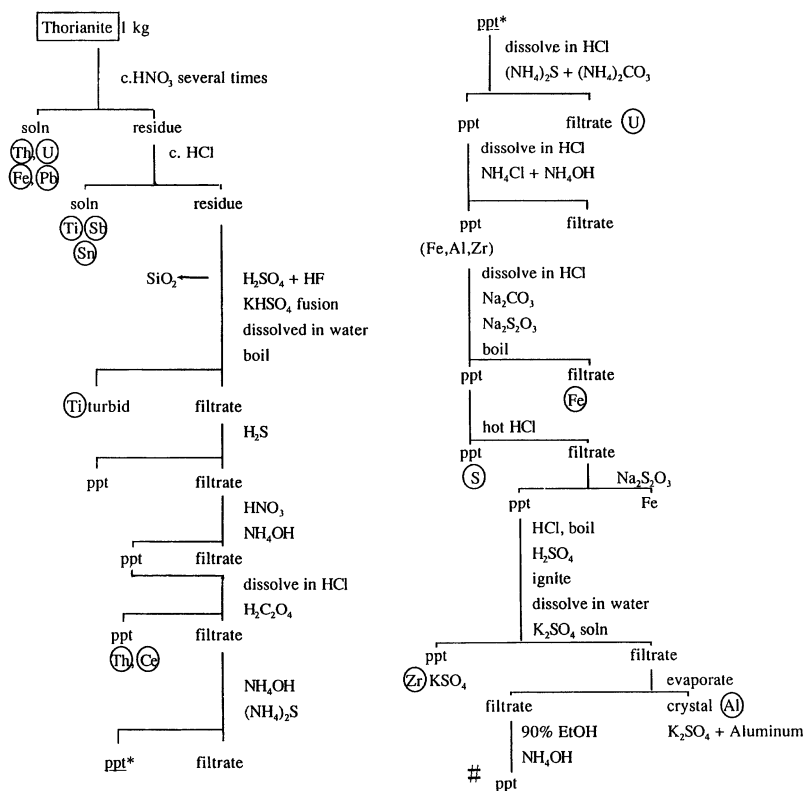


Fig. 3. Chemical procedures for thorianite analysis. Nipponium goes to the position (#) at the right side bottom.

from the First High School to the Tokyo Higher Normal School and continued his study of the new element.

Ogawa made a serendipitous discovery after his return to Japan. He found that the element was contained in reinite (FeWO₄) and in molybdenite (MoS₂) as confirmed by spectroscopy. He published two reports on the new element 'nipponium' in "Chemical News" in 1908.^{12,13} (Duplicate reports appeared in the Journal of the College of Science, the Imperial University of Tokyo in the same year.)

In the first report he described the following results (after Ogawa's original description).

1. The hydroxide precipitated by ammonia in the presence of ammonium chloride, has an almost white colour with a pale yellow tinge. It soluble in alkali, but not so readily as aluminium hydroxide.
2. On drying at 100 °C it becomes nearly black. The ignited oxide has a dark brown colour, and is insoluble in acids, but becomes soluble after fusion with hydrogen potassium sulphate.
3. A solution of hydroxide in hydrochloric acid has a yellowish green colour and gives a chocolate brown

precipitate on boiling with sodium thiosulphate. (For simplicity 4–9 are omitted here.)

10. The chloride gives a characteristic line, besides two other feebler lines, in the green-blue part of the spectrum, having a wavelength of 4882 (he dropped its unit).

11. The equivalent weight of the element is about 50, this element probably filling the gap between molybdenum and ruthenium and having an atomic weight of about 100.

12. The element appears to exist in two degrees of oxidation. The lower oxide behaves as a basic oxide and comes along with alumina in the ordinary course of analysis. Its separation from the latter is, indeed, very difficult; conversion into the volatile chloride by heating in a current of chlorine gas and carbon tetrachloride vapour being at present, the only means of separation. The higher oxide behaves as an acidic oxide, similar to molybdenum trioxide, and is reducible into the basic oxide by means of zinc and hydrochloric acid.

At the end of the paper he wrote:

"The name Nipponium, with the symbol Np, was

once suggested by Sir WILLIAM RAMSAY, and this name will be provisionally employed to indicate the new element.”

The second paper cannot be as clearly understood as the first one. Ogawa used the title “Preliminary note on a new element allied to molybdenum.” It is not clear whether he found one more new element or whether “a new element” means nipponium with another valence. It may be interpreted that this element is the same as nipponium but difficult to separate from molybdenum. In this report, the expression ‘a double silicate of zirconium and nipponium’ is judged to be a mistake by him. This is because a small portion of zircon (zirconium silicate) crystals mixed in thorianite was confirmed by Kobayashi in 1912,¹⁴⁾ and no nipponium was detected by him in these crystals. The work of Kobayashi was done under the guidance of Ogawa, who had to recognize the evident experimental facts on the double silicate of zirconium and nipponium. Description related to this zircon problem appears again in Section 5.

4. Ogawa's glory and misfortune of nipponium

Once Ogawa's papers had been published, a big sensation arose around him. Professor Joji Sakurai of the Imperial University of Tokyo was considering Ogawa for the first Prize of the Chemical Society of Tokyo, and asked Ramsay and Divers, who knew well Ogawa's scientific achievement, for their opinions. Ramsay agreed with Sakurai, but Divers wrote him a letter (July 20, 1908) as follows.¹⁵⁾

“Turning to my last letter about Nipponium I have to add that I find that Ramsay had committed himself to view of the position of this element in the periodic series given in Ogawa's paper. I do not agree and told Ramsay so plainly. Further research and the isolation of the higher oxide or its salts must settle the point.”

As became known later, Divers gave a favorable opinion on Ogawa's work to Sakurai, but it was not accepted by Sakurai. Loring¹⁶⁾ adopted nipponium (symbol: Np) in his periodic table in 1909. The name of nipponium had begun spreading internationally.

Ogawa was awarded the Sakurai Medal of the Chemical Society of Tokyo for the first time in 1910. He received a degree of Doctor of Science in the same year. Then, in 1911, he was promoted to

Professor of Chemistry, Tohoku Imperial University, in Sendai, Japan. He served as the Dean of its Science College (Photo 1).

In Sendai, he gave thorianite to his assistant Shin-ichi Aoyama, a young assistant professor Matsusuke Kobayashi and a graduate student Heihachiro Ono, but they failed to concentrate and detect nipponium probably because of a lack of skill in separating a micro amount of material from a large quantity of thorianite. Only Ogawa could separate it, and he continued his study day and night. However, Ogawa himself was still worried about the atomic weight problem of nipponium.

Meanwhile, the atomic number concept proposed by Moseley (1913) replaced atomic weight in determining the order of elements in the periodic table. Moreover, it became known that an element emitting X-rays can be identified by measuring its characteristic X-rays. Moseley began to apply this method to elemental analysis, but his death (1914) in the First World War delayed its progress.

Ogawa obtained this information and considered applying X-ray spectroscopic identification of elements to determining the position of nipponium in the periodic table. He wished to visit Europe after the World War I and received permission to do so from the Japanese Government, but it happened that he was elected President of Tohoku Imperial University in 1919. He cancelled his plan to go abroad. In that year, he told Makita, one of his former students, about his plan to use X-ray spectroscopy, showing him a lump of about 1 cm³ in size, which shone brilliantly.¹⁷⁾ He said:

“Nipponium is in it. I wish to subject it to X-ray inspection.”

Of course X-ray inspection means analysis by using X-ray spectroscopy. There were, however, no X-ray analysis apparatus available for chemists in Japan; nevertheless, Ogawa intended to put his plan into action. He supported Aoyama's stay in Europe, which included learning about X-ray spectroscopic analysis. After Aoyama came back to Japan, he bought an X-ray apparatus. Ogawa asked him to measure his nipponium sample. The result showed what nipponium was, but Ogawa's sudden death in 1930 prevented the publication of the measurement results.

Details of these scientific measurements are described later in this paper (Section 8).



Photo 1. Masataka Ogawa (1865–1930)

5. Various opinions on nipponium

After Ogawa died in 1930, his work on nipponium appeared to fall into almost complete neglect. Element 43, technetium, was known to be a radioactive element and not present in nature with the exception of fission products in uranium ores. This knowledge expelled nipponium as if it were a phantom. But a few researchers sensed some validity regarding this element.

1. Tiede at Berlin University told Toshiyuki Majima that nipponium might be rhenium when the latter visited him in 1938.¹⁸⁾
2. Goldschmidt, a famous geochemist, wrote in his book "Geochemistry" (1954)¹⁹⁾ that "a supposed new element 'nipponium' reported many years ago, may have been a mixture of oxides of rhenium and molybdenum, as it had been isolated from Japanese molybdenite and the description fit such a mixture."
3. Onishi, Professor Emeritus of University of Tsukuba, pointed out that nipponium might be rhenium from its optical spectrum data, but could not confirm it in his short note²⁰⁾ in 1990.

Contrary to the above opinions suggesting that nipponium was rhenium, de Hevesy²¹⁾ (Nobel Prize 1943), who discovered hafnium in 1923, reported as follows (originally written in French).

"Some years ago OGAWA considered that in thorianite he had discovered the silicate of a new element, nipponium. M.R.-B. Moore, had kindly supplied us some of crystals of the silicate of nipponium obtained from Ogawa. The crystals were essentially composed of zirconium silicate with content of 2% hafnium."

It is necessary to add some comments to this description. Ogawa had told Majima previously that he had not given his nipponium sample to Moore.²²⁾ According to his second report published in *Chemical News*, Ogawa had found zircon-like crystals in thorianite. He wrote about these crystals as if they were double silicate of zirconium and nipponium, but this description is judged to be his mistake. Kobayashi¹⁴⁾ analysed them accurately later, and proved that they had a composition of zirconium silicate: namely zircon. (This was published only in Japanese journal.) Ogawa had probably left those crystals at University College, London. After Ogawa returned to Japan, Moore went there and, being interested in the name of nipponium, took the crystals with him when he returned to the USA. The crystals were not compounds of true nipponium but of zirconium (zircon), which usually contains a small amount of hafnium. Therefore, de Hevesy measured zircon in the name of nipponium silicate, and found zirconium containing a small amount of hafnium.

This can explain why de Hevesy detected hafnium in his 'nipponium silicate'. It is a matter of course that hafnium is found in zircon when zircon (zirconium silicate) is analyzed precisely. Therefore, thorianite contains hafnium as an impurity of zircon which is mixed in its ores. The above explanation can be applied to Fig. 2 in which hafnium is expected to be one of the new elements by Ramsay and Ogawa.

The readers of the present paper can understand that nipponium is not hafnium in spite of the X-ray analysis by de Hevesy. Accordingly, Spronsen²³⁾ and Trifonov and Trifonov²⁴⁾ who followed de Hevesy and regarded nipponium as hafnium all misunderstood the true nipponium.

6. Reconsideration of the nipponium discovery

Great progress has been made in all the aspects of chemistry since Ogawa published his papers on nipponium in 1908. The present author, as a

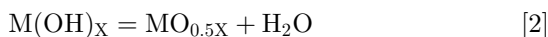
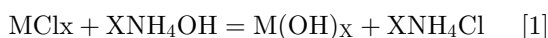
specialist on the element 43 (Tc) had been considering that Ogawa's work be examined in detail from a modern chemical viewpoint. Then the chance to do this came when the present author was invited to present a paper at the symposium "Discovery of Elements" which was held at the Leuven University, Belgium in 1996.

The contents of the paper were published the next year in *Radiochimica Acta*, a radiochemistry journal.²⁵⁾ It discusses in detail nipponium from a modern chemical viewpoints and concludes that nipponium was element 75, namely present-day rhenium.

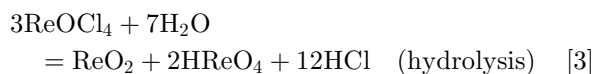
A comparison of nipponium with rhenium is given in Table 1 which shows the following facts.

1. Ogawa reported that the spectrum consisted of three lines among which the strongest one was at 4882 ± 10 Å. This description fits the rhenium line being at 4889.17 Å.

2. Ogawa calculated an equivalent weight of nipponium as 50.3, by a two-step reaction starting from its chloride (0.1092 g) and resulting final oxide (0.0742 g). To obtain its atomic weight, the equivalent weight should be multiplied by its valence (X).



He assumed $X = 2$; this means that divalent M (nipponium) is assumed. However, divalent technetium and rhenium are usually unstable, and moreover, the starting material should not be MCl_2 but should be MOCl_4 in the chlorination procedure used in today's chemistry. For oxychloride MOCl_4 the processes [1] and [2] should be changed as follows (replacing M by Re hereafter),



The above reaction gives stoichiometrically the same resultants as the oxidation reaction followed by disproportionation.



This process [5] is finally regarded as replacement of Cl_4 by O_2 surrounding a [ReO] core.

As in the treatment of Eqs. [1] and [2], therefore, multiplying $X = 4$, the [ReO] core weight Y can be calculated to be 201.2. The atomic weight

Table 1. Comparison of nipponium with rhenium

	Nipponium	Rhenium
Optical spectrum	4882 ± 10 Å	4889 Å
Atomic weight	100 185.2*	186.2
Occurrence	rich source molybdenite	source ore molybdenite
Properties, reactions	hydroxide, oxide metal: similar	hydroxide, oxide metal: similar

*recalculated by the author

of Re is, of course, $Y - W_O$, where W_O is the atomic weight of oxygen. Thus, the calculation gives 185.2 as the atomic weight of rhenium, being close to its present atomic weight of 186.2.

3. Ogawa stated that Japanese molybdenite contained a comparatively large amount of nipponium. According to Terada *et al.*²⁶⁾ the content of rhenium in Japanese molybdenite ranges from 15 to 3000 ppm. This fits Ogawa's description. At present the source ore of rhenium is mainly molybdenite. The reason why molybdenite (MoS_2) concentrates rhenium is now clear: because of the similarity of ionic radii of molybdenum(IV) and rhenium(IV), the latter can easily replace molybdenum.

4. Ogawa observed some properties and characteristic reactions of nipponium, among which the data of hydroxide, oxide and metal resembled those of rhenium.

As seen in Table 1, it is clear that nipponium is similar to rhenium. The most important similarity is in its optical spectrum. No other metals have a spectral line at this position. From this point it could be said that nipponium was a new element discovered in 1908. It would probably have been if Ogawa had declared his discovery of the new element first, and then determined its atomic weight more accurately after making a study of higher oxide(s) as recommended by Divers, who had abundant experiences in the chemistry of oxides and oxyacids.

7. Experimental approach to nipponium-related materials

The author thought that it was necessary to find Ogawa's original sample(s) of nipponium and to measure its optical spectrum and subject it to radioactivation analysis. This, of course, would

elucidate nipponium from a modern chemical viewpoint. However, none of his samples of nipponium could be found anywhere.

In his nipponium study, Ogawa was mainly engaged in analyses of three kinds of minerals: (1) thorianite given him by Ramsay, (2) Japanese molybdenite and (3) iridosmin obtained from Hokkaido.²⁷⁾

The composition of a thorianite sample obtained from Nakatsugawa Mineral Museum was analysed using an electron probe microanalyser (EPMA). The EPMA apparatus was from the Institute for Material Research, Tohoku University, and used for routine analysis of various materials (its accuracy in quantitative analysis is not particularly high). The results of this analysis of thorianite are shown in Table 2. The main components of this mineral were shown to be thorium and uranium, with impurities of Pb, Fe, Al, Ca, Ce, Si, and Nd included in it. Other minor elements (below 1 wt%) were Na, S, Cl, Y, Zr, La, Pr, Sm, Gd, Dy and Re.

A sample of molybdenite obtained from Okawame Mine in Iwate Prefecture was analysed by using the SPring-8 Facility in Hyogo Prefecture, Japan. The energetic and high intensity photon beams generated by the facility make it possible to excite inner shell electrons of heavy atoms such as rhenium. Therefore, molybdenite was irradiated for analysis and the resulting spectrum is shown in Fig. 4. As is seen in the figure, K X-rays of rhenium and tungsten appeared very clearly.²⁸⁾ The sample was estimated to have about 500 ppm for rhenium and 300 ppm for tungsten, which compared reasonably with values of Terada and coworkers.²⁶⁾

In the last period of his research, Ogawa was extracting nipponium from platinum group element ores, one of which was iridosmin composed of iridium and osmium. Probably because of its resemblance to neighboring transition elements, he was trying to look for nipponium in this osmium containing mineral. Figure 5 details the various possible routes²⁹⁾ to attain Elements 43 and 75, which were unknown in 1908. Shigenori Aomine, Professor Emeritus of Kyushu University, who is the husband of Shige, the fourth daughter of Masataka Ogawa, fortunately preserved two crucibles used by Ogawa as memorials of his father-in-law. Professor Aomine kindly gave the author enough time to scientifically inspect these crucibles

Table 2. Analysis of thorianite

	Element	Wt%	Element	Wt%
Main component	Th	54.4	U	20.5
Impurities	Pb	4.9	Ca	2.7
	Fe	3.9	Ce	2.7
	P	3.9	Si	2.0
	Al	2.8	Nd	1.1
Total				98.9

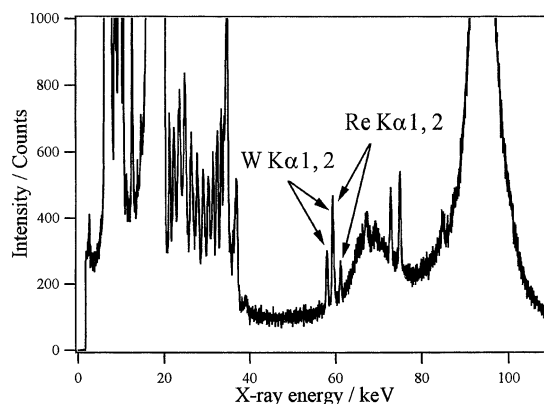


Fig. 4. Detection of rhenium and tungsten in molybdenite.

before offering them to Tohoku University Museum of History.

Analyses of the crucibles and also their contents were attempted. The elements detected using the photon beams of the SPring-8 Facility are shown in Table 3. Both crucibles were made of silver instead of platinum, because platinum crucibles are not suitable for the analysis of platinum group elements.

Interestingly, the material scratched from the inside of the larger crucible showed the presence of iridium, while no iridium was found in the smaller one. These results suggested that iridosmin was treated almost exclusively in the larger crucible. Osmium could not be detected because of its volatility. Barium and strontium usually come from sandy materials. (Light elements such as calcium and silicon are omitted in the present analysis.) Both crucibles contained mercury, suggesting that an amalgamation technique was adopted by the user. No rhenium was detected probably because of the very low concentration of this element in iridosmin.²⁷⁾

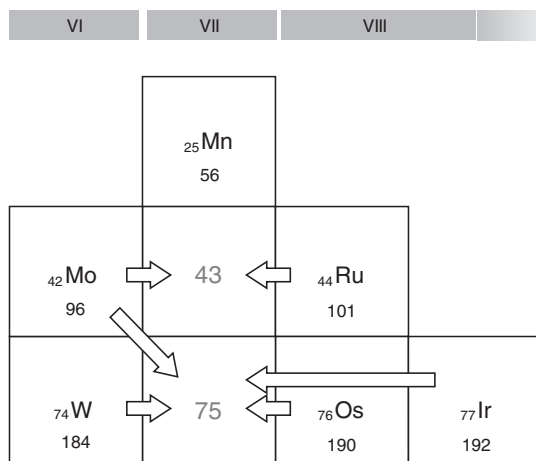


Fig. 5. Investigation routes to the element 43 and 75.
("Chemistry Today" 2004 No. 5, p. 39)

Table 3. Analytical results of two crucibles

	Larger crucible	Smaller crucible
Components of crucibles	major: Ag impurities: Ir	Ag Au
Substances on the inside surface	Au, Pt, Ir, Hg, Ag	Ba, (Sr), Hg, (Pt), Ag
(). elements which appear occasionally depending on sampling position		

8. Deciphering the X-ray spectrum in a photographic plate

As mentioned in section 4, Ogawa wished to subject his sample to X-ray spectroscopy which is applicable to determine the atomic number of an element. Using this method he would have been able to confirm the new element nipponium, of which valence and atomic weight were not fully known at that time.

Shin-ichi Aoyama, who was promoted assistant professor, went to Europe, and stayed at Niels Bohr's Institute in Copenhagen to study X-ray spectroscopy in 1926. Aoyama published an interesting paper³⁰⁾ on chemical shift of X-rays emitted from various chemical compounds with two Japanese students Kenjiro Kimura from the Imperial University of Tokyo and Yoshio Nishina from the Institute of Physical and Chemical Research.

When Aoyama returned to Japan in 1928, he wished to buy an X-ray spectrograph of the Siegbahn type with an attached recorder system.

Ogawa, as the president of Tohoku Imperial University, presumably pushed this plan to purchase such an expensive apparatus (in a request to the Ministry of Education). Aoyama was able to import the devices in 1929, and they became available for use in April, 1930.

Ogawa asked Aoyama to measure his samples related to nipponium. Their last conversation they had was recorded as follows.³¹⁾

Ogawa said: I wish you would take X-ray photographs of my samples, which will be prepared in a few weeks.

Aoyama replied: I shall do it with pleasure. But I hope that your health will be completely recovered.

This conversation was on July 10, 1930 when Ogawa was in bed at the university hospital. Ogawa suddenly died the next day. To the end, he had been an excellent experimentalist with a strong passion for chemical research. In this respect, he resembled William Ramsay.

The photographic plate (made of glass) shown in Photo 2 was left among Ogawa's mementos kept by his family. It is most probably conjectured that Aoyama took the photograph which Ogawa requested and handed it to him while he was still alive. Yoshiko Ogawa, wife of the late Prof. Shiro Ogawa who was the fourth son of Masataka Ogawa, kindly gave the author this photographic plate to inspect in 2003. No detailed explanation was attached to the plate, but some very important information was included in it.

In the photographic plate, there was a spectrum chart marked with Chinese characters and numerals (Arabic and Roman). This was interpreted as follows. The X-ray spectrum was taken by Aoyama in his response to Ogawa's requests. The Chinese characters read KINKEN, referring to the Institute of Iron, Steel and Other Metals (known now as the Institute for Material Research). This type of measurement was only done by Aoyama at that time. The numerals indicated reference elements added to (or mixed with) the sample. As the numeral VII or 7 is missing, these numerals could be read as 1(Rb), 2(Sr), 3(Y), 4(Zr), 5(Nb), 6(Mo) and 8(Ru). The Roman numbers (I, II, ..., VIII) attached to the peaks are similarly understood. This interpretation is reasonable because 7 (Tc) is lacking in nature and no reference to it was available in 1930. Other numerals 4 and 6 among

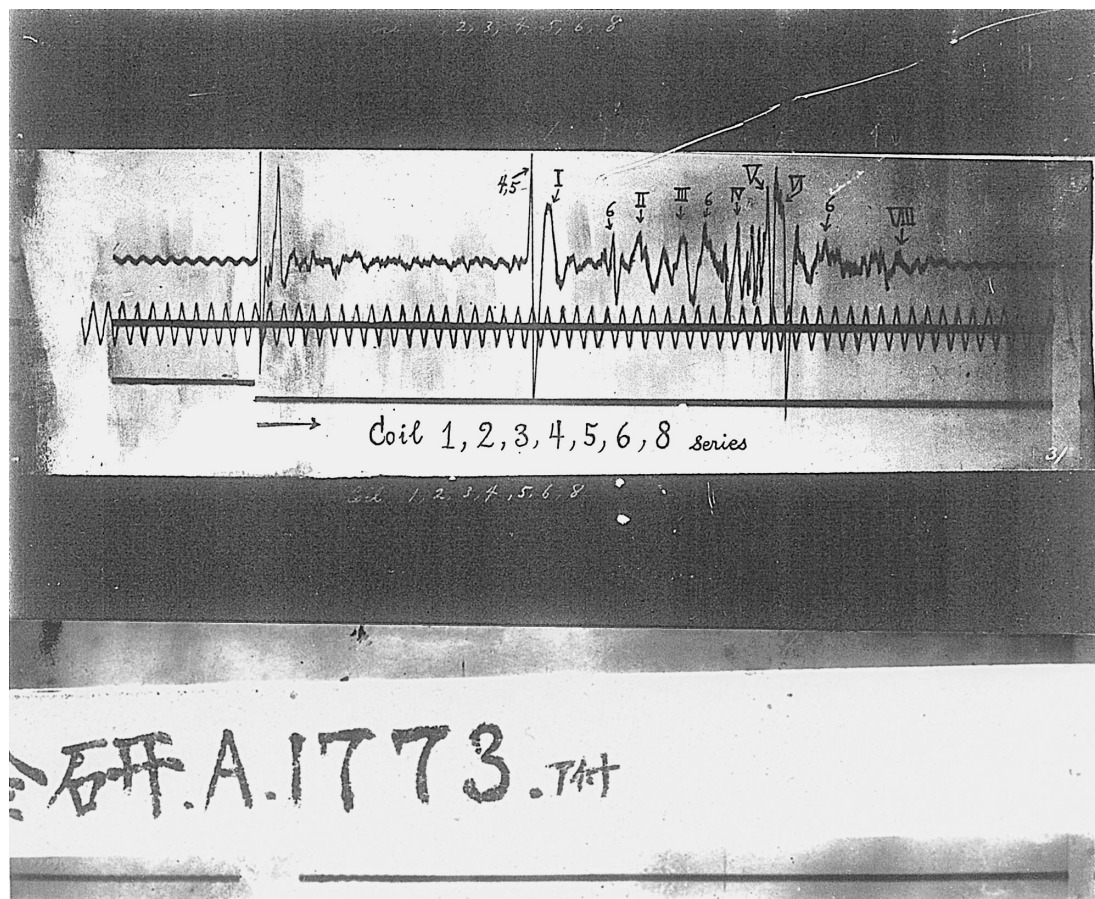


Photo 2. A photographic plate found among Ogawa's mementos

the (I, II, ..., VIII) series are assumed to be Th and U which remained in minor quantities in the sample. Additionally, the style of the Arabic numbers coincides with that of Aoyama's writings which are preserved at Tohoku University.

The spectrum in Photo 2 was deciphered by comparing the principal X-ray peaks of the above reference elements added to the sample with those peaks in the spectrum. The right side of the spectrum is shown in Fig. 6(a). The spectrum of the sample (upper part) is compared with the spectra (lower part) of the reference elements. The spectra shown in the lower part are synthetic ones based on the X-ray chart. Only K_α and K_β X-rays of the reference elements and L_α , L_β , and L_γ X-rays of thorium and uranium were taken into consideration. It is obvious that each principal peak of the reference elements has a corresponding peak in the measured spectrum. No noticeable peak is seen at the position of the K_β X-ray of element 43 (Tc).

There are two sharp peaks in the left side of the spectrum of the sample shown in Fig. 6(b), which can be clearly assigned to those of $L_{\beta 1}$ and $L_{\beta 2}$ X-rays of rhenium (with the wavelength corrected to the wavelength difference between $L_{\beta 1}$ and $L_{\beta 2}$ X-rays reported in the X-ray chart). From the figure it is obvious that element 43 is absent but, that element 75 is present in the sample.

The X-rays of thorium (black) and uranium (white-dotted black) in Fig. 6(a) indicated that these elements as the main components of thorianite remained at the last stage of separation in Ogawa's processes at University College, London. This meant that at Ogawa's request, Aoyama had examined his most important sample of nipponium by X-ray spectroscopy, which had been Ogawa's long-time wish.

The author wishes to further point out that the Th/U ratio 2 to 6 reported by Kobayashi¹⁴⁾ for thorianite fits the results of the X-ray measurement

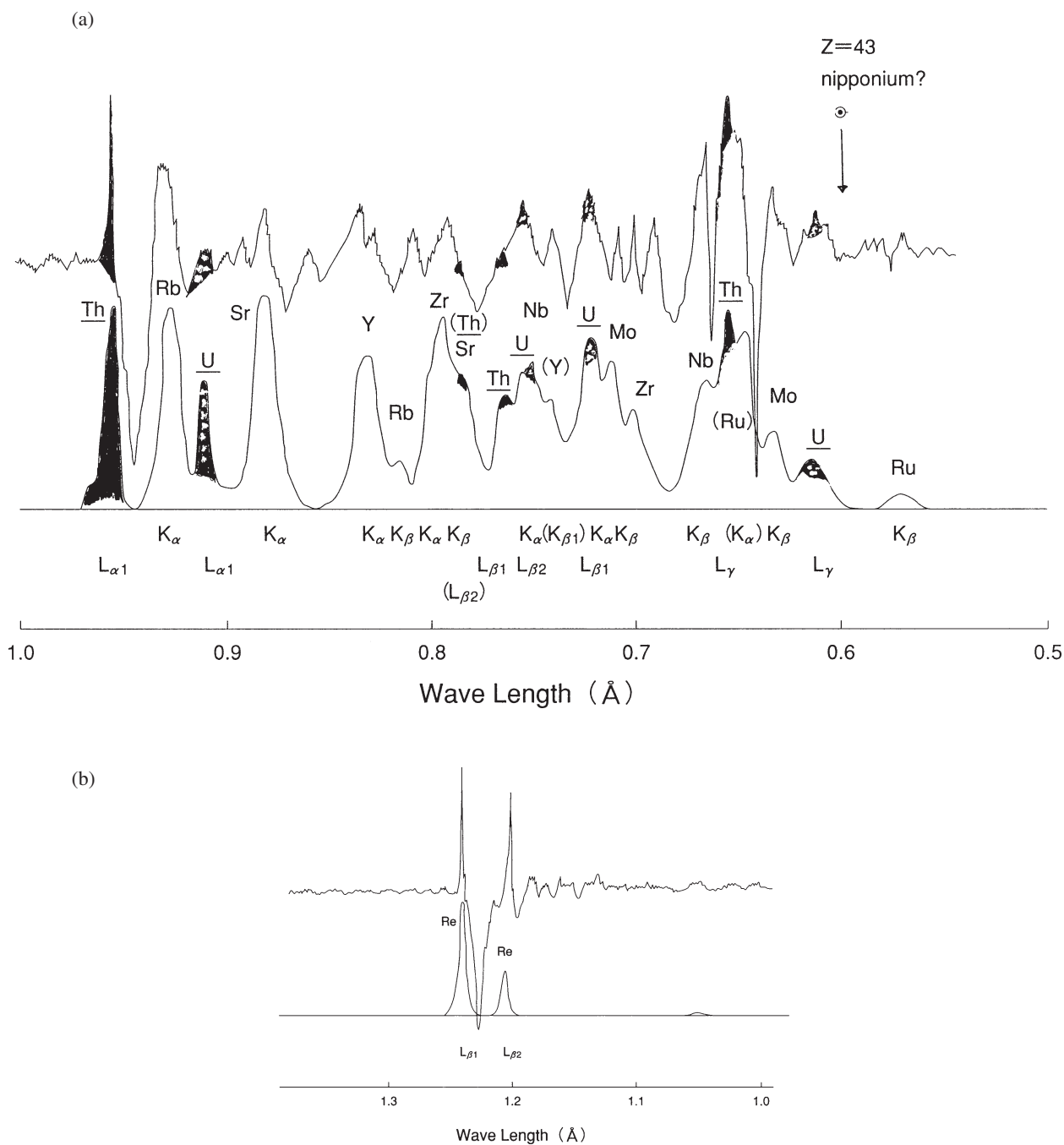


Fig. 6. Comparison of measured spectra (upper) with synthetic reference spectra (lower). (a) Analyses of the right side of the spectra, and (b) the left side of those in Photo 2.

in Fig. 6(a). Ogawa mainly used larger α -type crystals of thorianite for his analysis. Therefore, the measured ratio Th/U for $L_{\alpha 1}$ is nearly 6 of the α -type. (The data for finely powdered β -crystals are seen in Table 2.)

As described above, therefore, Ogawa's discovery of nipponium has been verified with clear evidences.

There is yet another appendage to this story. Ogawa asked Kenjiro Kimura at the Imperial

University of Tokyo to conduct on X-ray spectroscopic analysis of his nipponium sample, since Kimura had an X-ray analysis machine of Siegbahn type similar to Aoyama's. After taking the measurement, Kimura said:¹⁰⁾

"It [nipponium] was beautiful rhenium, indeed!"

This he told to his intimate friend Toshi Inoue at Gakushuin High School in Tokyo. The measurement was made in the late spring or early summer of 1930. (Ogawa probably wanted to confirm Aoyama's measurement. Aoyama did not use reference elements to rhenium as seen in Fig. 6.) The result, of course, disappointed Ogawa who had believed nipponium to be element 43. After some years had passed, Kimura asked his assistant Sakae Shinoda to separate rhenium from Japanese molybdenite. Shinoda obtained 0.5 g of rhenium metal from 1 kg of the ore,³²⁾ and subjected it to X-ray analysis. Kimura told Shinoda that this work should be published in "Nature", a famous English journal, but such was not realized. Presumably, Kimura wanted to confirm Ogawa's nipponium as element 75. Anyway, it was too late to claim nipponium as a new element because rhenium with $z = 75$ had already been discovered by Noddack and coworkers³⁾ in 1925 and confirmed further by extraction of visible amounts in 1927.³³⁾

9. Conclusion

In this paper, the author summarized considerations pertaining to 'nipponium discovery' by Masataka Ogawa in 1908. Based on similarities between nipponium and rhenium ($Z = 75$), the author argued in 1997 that nipponium was identical to rhenium.²⁵⁾ In 2003, a photographic plate that contains an X-ray spectrum was found among Ogawa's mementos preserved by his family. Deciphering this spectrum showed the presence of rhenium in the sample. This evidence was strongly supported by Kenjiro Kimura's measurement of a nipponium sample. Kimura said that "it was beautiful rhenium, indeed!". Therefore, the author came to the conclusion that nipponium and rhenium are no doubt the same element.^{34),35)}

To close this review the author wishes to emphasize that Masataka Ogawa succeeded in the separation of a new element 'nipponium', element 75, in 1908. Unfortunately, however, he placed it in a position between molybdenum and ruthenium

(today's Tc, $Z = 43$) in the periodic table of chemical elements. This was a pioneering work done by a Japanese chemist in the Meiji era (1868–1912). Instead of nipponium, rhenium was placed in the correct position 17 years later (Noddack and coworkers, 1925), but it is worthwhile noting that Ogawa first found a new route through molybdenite in attaining element 75. This route was utilized to extract the element rhenium in a visible amount and has also been used for industrial purposes.

10. Acknowledgement

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The author extends thanks to the members who cooperated in this work.

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References

- 1) Weeks, M.E. and Leicester, H.M. (1968) Discovery of Elements. J. Chem. Edu., Pennsylvania, U.S.A.
- 2) Trifonov, D.N. and Trifonov, V.D. (1980) Chemical Elements. Mir Publishers, Moscow.
- 3) Noddack, W., Tacke, I. and Berg, O. (1925) Die Ekamangane. Naturwiss. **26**, 567–574.
- 4) Perrier, C. and Segrè, E. (1937) Some chemical properties of element 43. J. Chem. Phys. **5**, 712–716.
- 5) Mendelejeff, D.I. (1871) Die Periodische Gesetzmaessigkeit Elemente. Ann. Chem. Pharm. (Suppl.) VIII, 133–229.
- 6) Morita, K., Morimoto, K., Kaji, D., Akiyama, T., Goto, S., Haba, H., Ideguchi, H., Kanungo, R., Katori, K., Koura, H. *et al.* (2004) Experiment on the synthesis of element 113 in the reaction $^{209}\text{Bi}(^{70}\text{Zn}, n)^{278}113$. J. Phys. Soc. Jpn. **73**, 2593–2596.
- 7) Travers, M.W. (1956) A Life of Sir William Ramsay. Edward Arnold, London.
- 8) Ogawa, M. (1904) A letter from Mr. M. Ogawa. J. Chem. Soc. Tokyo **25**, 542–543.
- 9) Ogawa, M. (1909) On a new element in Thorianite. J. Chem. Soc. Tokyo **30**, 1277–1299.
- 10) Yoshihara, H.K. (2000) Ogawa's discovery of nipponium and its re-evaluation. Hist. Scientia-

- rum **9**, 257–269. See ref. 12.
- 11) Kikuchi, Y. (2004) Joji Sakurai and his connections with British chemists. *J. Jpn. Soc. History Chem.* **31**, 239–267.
 - 12) Ogawa, M. (1908) Preliminary note on a new element in thorianite. *Chem. News* **98**, 249–251.
 - 13) Ogawa, M. (1908) Preliminary note on a new element allied to molybdenum. *Chem. News* **98**, 261–264.
 - 14) Kobayashi, M. (1912) On the composition of thorianite. *J. Chem. Soc. Tokyo* **33**, 549–556.
 - 15) J. Sakurai Documents, A letter to J. Sakurai from E. Divers, dated July 20, 1908 (The document belongs to Chemical Society of Japan).
 - 16) Loring, F.H. (1909) Atomic weights as mathematical functions. *Chem. News* **99**, 281–287.
 - 17) Makita, S. (1930) The new element is in it. *Memoirs of Alma Mater of Tohoku Chemistry Department* **8**, 27–28.
 - 18) Majima, T. (1954) Recollections of my life. *Kagaku no Ryoiki* **8**, 137–146.
 - 19) Goldschmidt, V.M. (1954) *Geochemistry*. Clarendon Press, Oxford, p. 645.
 - 20) Onishi, H. (1990) Was nipponium rhenium? *Chemistry and Chemical Industry (Kagaku to Kogyo)* **43**, 1717.
 - 21) de Hevesy, G. (1925) *Recherches sur le Propriétés du Hafnium*. Kgl. Danske Videnskab. Selskab. Math-Fys. VI,7, p. 143.
 - 22) Majima, T. (1925) Report on travel in foreign countries. *Memoirs of Alma Mater of Tohoku Chemistry Department* **2**, 1–7.
 - 23) von Spronsen, J.N. (1969) *The Periodic System of Chemical Elements—A History of the First Hundred Years*. Elsevier, Amsterdam, p. 227.
 - 24) Trifonov, D.N. and Trifonov, V.D. (1982) *Chemical Elements* (English ed.). Mir Publishers, Moscow, p. 201.
 - 25) Yoshihara, K. (1997) Nipponium, the element ascribable to rhenium from the modern chemical viewpoint. *Radiochim. Acta* **77**, 9–13.
 - 26) Terada, K., Osaki, S., Ishihara, S. and Kiba, Y. (1971) Distribution of rhenium in molybdenite from Japan. *Geochem. J.* **4**, 123–141.
 - 27) Shibata, Z. (1940) On nipponium. *Kagaku Gaho*, no. 10, 24–27.
 - 28) Yoshihara, K., Nakai, I., Terada, Y. and Kaji, M. (2002) Nipponium studies by Masataka and Eijiro Ogawa. *J. Jpn. Soc. Hist. Chem.* **29**, 209–221.
 - 29) Yoshihara, K. (2004) Discovery of nipponium. *Chemistry Today*, no. 5, 36–41.
 - 30) Aoyama, S., Kimura, K. and Nishina, Y. (1927) Die Abhängigkeit der Roentogenabsorptionsspektren von der chemischen Bindung, *Z. Phys.* **44**, 810–833.
 - 31) Aoyama, S. (1930) Conversation one day before Prof. Ogawa's death. *Memoirs of Alma Mater of Tohoku Chemistry Department* **8**, 2–4.
 - 32) Yoshihara, K. (1999) Nipponium. *Isotope News*, no. 10, 26–29.
 - 33) Noddack, I. and Noddack, W. (1927) Darstellung und einige chemischen Eigenschaften des Rhenium. *Z. Phys. Chem.* **125**, 264–274.
 - 34) Yoshihara, H.K. (2004) Discovery of a new element 'nipponium': Re-evaluation of pioneering works of Masataka Ogawa and his son Eijiro Ogawa. *Spectrochim. Acta* **B59**, 1305–1310.
 - 35) Yoshihara, H.K. (2005) Ogawa family and their 'nipponium' research: Successful separation of element 75 before its discovery by Noddacks, *Hist. Scientiarum* **15**, 177–190.

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Profile

Kenji Yoshihara was born in Niigata City in 1929. He was a middle school boy in August of 1945 when World War II ended and Japan was defeated after the atomic bombing of Hiroshima and Nagasaki. At that time, all the citizens in Niigata City were evacuated by the order of the mayor who feared that Niigata would be the third target of the nuclear weapon. The memory of that experience has stuck strongly in the author's mind.

After the author graduated from the Department of Chemistry, Faculty of Science, Tohoku University in 1953, he engaged in the measurement of radioactive materials at the Government Electrotechnical Laboratory in Tokyo from 1954 to 1957. Then, he joined the Japan Atomic Energy Research Institute, where he engaged in the production of radioisotopes (1957–68). Hot atom chemistry was his special field of research, and the first determination of 'appearance energy' for solid hot atoms was reported by him. The author returned to Tohoku University to carry out radiochemistry research and education in 1968, and he became professor of the University in 1982.

He was interested in technetium chemistry, and he studied the first radiosynthesis of technetium phthalocyanin using the cyclotron at Kernforschungszentrum, Karlsruhe, Germany when he stayed there as a guest professor in 1973. The rhenium compound was also similarly synthesized there. He organized an international symposium on the "Behavior and Utilization of Technetium" in 1993 just before his retirement from Tohoku University.

He then devoted much effort to solving the puzzle of nipponium, which was reported many years ago by Masataka Ogawa, the fourth President of Tohoku University. This element was placed incorrectly in the position of technetium ($Z = 43$) in Ogawa's paper, and his work was subsequently ignored. However, a clear verification of his long-ignored discovery has now been made. At present, it is internationally recognized that nipponium was identical to rhenium based on the scientific evidence described in this paper. He is the recipient of the Prize of the Japanese Society for the History of Chemistry in 2008. He is the author of the following books: "Periodic Table with Nuclides and Reference Data", Springer Verlag, Heidelberg, 1985; "Chemical Applications of Nuclear Probes", Springer Verlag, Heidelberg, 1990; and "Technetium and Rhenium", Springer Verlag, Heidelberg, 1996.

